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SALES hereby certify that annexed is a true copy of the Provisional specification  
in connection with Application No. 2003906420 for a patent by  
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
ORGANISATION as filed on 21 November 2003.



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AUSTRALIA  
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PROVISIONAL SPECIFICATION

**Applicant(s) :**

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ORGANISATION

**Invention Title:**

METHOD OF PRODUCING TITANIUM-ALUMINIUM COMPOUNDS

The invention is described in the following statement:

## A METHOD AND APPARATUS FOR THE PRODUCTION OF METAL COMPOUNDS

### Field of the Invention

5       The present invention relates to a method and apparatus for the production of metal and metal compounds and, particularly, but not exclusively, to a method and apparatus for production of titanium-based alloys and intermetallic complexes, and more particularly, but not  
10 exclusively, to a method and apparatus for the production of titanium-aluminium based alloys and intermetallic complexes, and more particularly, but not exclusively, to a method and apparatus for the production of titanium-aluminium based alloys and intermetallic complexes in a  
15 powder form.

### Background of the Invention

20       Titanium-aluminium alloys and inter-metallic compounds (generically termed herein "titanium-aluminium compounds") are very valuable materials. However, they are difficult and expensive to prepare, particularly in the preferred powder form. This expense of preparation limits wide use of these materials, even though they have  
25 highly desirable properties for use in areas such as automotive, aerospace and others.

      Titanium minerals are found in the form of a very stable oxide ( $\text{TiO}_2$ ). Common processes for the production of titanium are the Kroll process and the Hunter process.  
30       The Kroll process requires the use of magnesium as a reducing agent to reduce  $\text{TiCl}_4$  (prepared from the oxide by a pre-process of chlorination) to produce the Ti metal. The Hunter process requires the use of sodium as the reducing agent. Because  $\text{TiCl}_4$  is still thermodynamically  
35 stable, highly reactive reducing agents such as magnesium or sodium are required to produce titanium metal out of  $\text{TiCl}_4$ . Such highly reactive reducing agents are difficult

and expensive to handle. As the magnesium chlorides in the case of the Kroll process are stable up to temperatures in excess of 1300 K, the product is often in the form of a Ti sponge mixed with  $MgCl_2$  and remnants of Mg and  $TiCl_3$ . To obtain pure Ti, the product requires extensive post-processing, including washing and melting in a vacuum arc furnace to remove all impurities. This contributes to the present high cost of the production of titanium.

According to existing technologies for production of titanium alloys such as Ti-Al-V, and intermetallic compounds such as  $Ti_3Al$ ,  $TiAl$ ,  $TiAl_3$ , Ti-Al-(Cr, Nb, Mo, etc) and alloys based on these compounds, sponges or ingots of the required metals in appropriate amounts are melted together, hence adding to the production cost. For production of powder of these titanium alloys and intermetallic compounds, further processing is usually required, further compounding the already high production cost.

Prior Al based processes for manufacturing of Ti-Al compounds include starting from Al powder and Ti powder (references: (I.Lu, M.O. Lai and F.H. Froes, JOM, Feb 2002 p62) and (N. Bertolino et al., Intermetallics, vol 11,2003 p 41) and reduction of  $TiCl_4$  with AlCl (US patent application US2002/0184971 A1). For the first process where starting materials are Al and Ti powders, the powders are usually mechanically milled to make a uniform mixture followed by heating in a furnace. The resulting materials are at best in the form of solid lumps and this process is usually unable to produce fine powder. Furthermore, the resulting compounds often require heat treatment to produce the required material properties. For the second process, Al metal is heated in the presence of chlorine at temperature around 1200 C to produce gaseous AlCl that is then reacted with  $TiCl_4$  in the gas phase to produce powders of titanium aluminides. Both these processes are quite complex and costly.

Over the past several decades, there have been extensive attempts made to replace the existing Kroll and Hunter technologies using techniques such as electrowinning, plasma-hydrogen and also aluminothermic reduction.

Attempts have been made to use hydrogen plasma for reduction of titanium chloride in a plasma atmosphere, as possible replacement of the existing Kroll and Hunter processes. However, reduction of  $TiCl_4$  by hydrogen is difficult due to unfavourable thermodynamic characteristics, as chlorine preferably reacts with titanium in the reverse reaction to produce titanium chlorides, hence degrading the quality of the produced Ti powder and limiting the efficiency of the hydrogen plasma route. In a recent process disclosed in US patent 5,935,293, a fast quench reactor was used to cool down the plasma in order to prevent recombination processes leading to formation of titanium chlorides. According to the description in US patent (5,935,293), the process is highly energy expensive relative to the existing Kroll technology.

In a more recent process (G.Z. Chen, D.J. Fray and T.W. Farthing, Nature, vol 407 (2000) 361), Chen et al. made titanium sponge directly from the oxide by reduction in a molten calcium chloride salt. Oxygen from the titanium oxide recombines with carbon at an anode to form  $CO_2$ . The composition of the titanium sponge produced corresponds to the composition of the starting minerals. The process is yet to be demonstrated on an industrial scale.

Attempts have been made to use aluminium as a reducing agent for  $TiCl_4$  in plasma systems. For reduction of  $TiCl_4$  using aluminium, the products would be in the form of a solid phase titanium-aluminium intermetallic compounds mixed with aluminium chloride and some residual titanium dichloride. A description of various attempts using aluminium together with a description of the

thermodynamics of the process are given by Murphy and Bing (High Temp. Chem. Processes, vol 3, 365-374, 1994).

Because of difficulties associated with gas phase reactions it has not been possible to produce titanium  
5 and/or titanium-aluminium compounds by direct aluminothermic reduction of titanium chlorides.

#### Summary of the Invention

In accordance with a first aspect, the present invention provides a method for the production of titanium  
10 compounds, comprising the steps of mixing a precursor material of titanium subchloride with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium chlorides and titanium compounds.

Titanium subchloride may include titanium trichloride  
15 and/or titanium dichloride.

Titanium compounds may include titanium alloys and/or titanium/metal intermetallic compounds.

Preferably, the titanium compounds may include titanium-aluminium alloy and/or titanium-aluminium  
20 intermetallic compounds.

Preferably, where titanium trichloride is used as the subchloride the titanium trichloride is prepared from titanium chloride ( $\text{TiCl}_4$ ). Preferably, the  $\text{TiCl}_3$  is prepared by reduction of  $\text{TiCl}_4$ . Preferably, the reduction is  
25 aluminium or with hydrogen.

The precursor material may include titanium diochloride ( $\text{TiCl}_2$ ).

Preferably, the reaction conditions are arranged to favour the forward reaction to form the aluminium  
30 trichloride and titanium compounds, and reduce the reverse reaction. Preferably, this is achieved by removing aluminium trichloride from a reaction zone where the aluminium and precursor material are reacting.

The precursor materials may include other metals  
35 and/or metal halides and products may include titanium alloys or intermetallic compounds. For example the precursor material may include vanadium subchlorides, such

as vanadium trichloride and/or vanadium dichloride, and the products may include titanium-aluminium-vanadium alloy and/or intermetallic compounds and/or titanium-vanadium alloy and/or intermetallic compounds.

5       The precursor material may include chromium halide, such as chromium chloride, and the products may include a titanium-aluminium-chromium alloy and/or intermetallic compounds and/or titanium-chromium alloy and/or intermediate compounds.

10       The precursor material may include one or more chlorides of elements such as (Cr, Nb, Mo, Zr, Si, B, etc), and the products may include a titanium-aluminium- (Cr, Nb, Mo, Zr, Si, B, etc) alloy.

15       In accordance with a second aspect, the present invention provides a method for the production of metal compound, comprising the steps of mixing a precursor material of metal halide with aluminium and heating the mixture to a temperature sufficient such that the precursor material reacts with the aluminium, resulting in  
20       the formation of aluminium halide, and arranging the conditions to favour the forward reaction to form the aluminium halide and reduce the reverse reaction.

25       Preferably, the step of arranging reaction conditions includes the step of driving the aluminium halide away from a reaction zone where the aluminium and precursor material are reacting. Continuous removal of the aluminium halide facilitates the forward reaction.

Preferably, the halide is a chloride.

30       Preferably, the metal halide is titanium halide and the product is titanium compounds.

35       In accordance with a third aspect, the present invention provides an apparatus for the production of a metal compound, comprising a reaction vessel including a reaction zone within which a precursor material of metal halide is mixed with aluminium, the mixture being heated to a temperature sufficient such that the precursor material reacts with the aluminium to result in the

formation of aluminium halide and a product, and a first condensation zone arranged to be operated to a temperature such that the aluminium halide condenses in the first condensation zone.

5        Preferably, the reaction vessel also includes a second condensation zone where a metal halide is arranged to condense. Preferably, the metal halide may be provided back into the reaction zone from the second condensation zone.

10       Preferably, the reaction zone operates at a temperature T1 and the first condensation zone at a temperature T2 which is lower than the temperature T1. The second condensation zone preferably operates at a temperature T3 which is between T1 and T2.

15       The precursor material may be a material containing titanium as a component. The precursor material, preferably includes titanium trichloride and/or titanium dichloride.

20       Preferably, where the precursor material includes titanium trichloride and where the apparatus includes a first condensation zone that operates at temperature T2, T2 is preferably below 200C, wherein gaseous aluminium trichloride emanating from the reaction zone is condensed.

25       Preferably, where the apparatus includes a second condensation zone, T3 is below 500C where and titanium trichloride escaping from the reaction zone is recondensed at the second condensation zone. Preferably the second condensation zone is located between the reaction zone and the first condensation zone.

30       Preferably, the apparatus includes a heating arrangement for heating the precursor material. Preferably, openings are provided for the introduction of further gases for further reactions. Openings may also be provided to evacuate the vessel to a low pressure.

35       Preferably, the apparatus of this aspect of the invention is suitable for implementing the method of the first and second aspects of the invention discussed above.



In accordance with a fourth aspect, the present invention provides a method for the production of vanadium compounds, comprising the steps of mixing a precursor material of vanadium trichloride with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium chlorides and vanadium compounds.

The vanadium compounds may include vanadium-aluminium alloys and/or vanadium aluminium intermetallic complexes.

In accordance with a fifth aspect, the present invention provides a method for the production of zirconium compounds, comprising the steps of mixing a precursor material including zirconium trichloride and aluminium and heating the mixture to trigger reactions leading to the formation of aluminium chlorides and zirconium compounds.

The zirconium compounds may include zirconium-aluminium alloys and/or zirconium-aluminium intermetallic complexes.

In accordance with a sixth aspect, the present invention provides a method for the production of titanium and/or titanium compounds, comprising the steps of mixing a precursor material including titanium tri-chloride with a reducing agent and heating the mixture to trigger reactions leading to the formation of chlorides and titanium and/or titanium compounds.

In accordance with a seventh aspect, the present invention provides a method for the production of compounds of nickel aluminides, comprising the steps of mixing the precursor material including nickel chlorides with aluminium and heating the mixture to trigger reactions leading to the formation of the alloys or the intermetallic compounds. Preferably, the nickel aluminides are  $Ni_3Al$ ,  $NiAl$  and  $NiAl_3$ .

### Brief Description of the Drawings

Features and advantages of the present invention will become apparent from the following description of

embodiments thereof, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows the Gibbs energy of formation of  $\text{AlCl}_3(\text{g})$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_3 + \text{Ti-Al}$ ;

5 Figure 2 shows the total Gibbs free energy for reactions leading to formation of Ti-metal based compounds;

Figure 3 illustrates the equilibrium composition of  $\text{TiCl}_4$  - Hydrogen plasma at temperatures of between 300K and 5000K;

10 Figure 4 is a schematic diagram of an apparatus for implementing a process in accordance with an embodiment of the present invention;

Figure 5 is a schematic diagram of a further embodiment of an apparatus for implementing a process in accordance with an embodiment of the present invention;

15 Figure 6 is a schematic flow diagram showing production of Ti-Al powder from  $\text{TiCl}_4$  starting materials; and

20 Figure 7 illustrates the Gibbs free energy for half reactions leading to the formation of titanium-tetrachloride.

#### Description of Preferred Embodiments

25 The following description is of preferred embodiments of processes for producing metal compounds, including fine powder and ingots with specific compositions. The processes are useful for production of forms of metals such as Ti, V, Zr, Ni, together with alloys and

30 intermetallic compounds of these metals with a controllable amount of aluminium. For example, Ti-Al,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}_3$ , Ti-Al-Cr and Ti-V-Al can be made with accurate various aluminium content. The relative amounts of titanium chlorides and aluminium are determined by the

35 required composition of end product. The process in one embodiment comprises the steps of preparing solid metal halides, mixing the halides with aluminium metal and

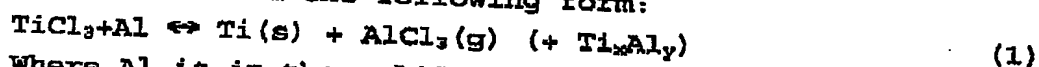
heating the mixture to a temperature T1 to trigger reactions leading to formation of aluminium chloride at a temperature (T1) above the boiling temperature of aluminium chlorides and condensing the aluminium chlorides away from the reaction zone at a temperature T2, T2 being less than T1. The driving of the aluminium chloride away from the reaction zone tilts the equilibrium of reaction in the forward direction i.e. to formation of aluminium chloride and metal (and other products depending upon reaction conditions and components). For titanium compounds, titanium subchlorides preferably titanium trichloride  $TiCl_3$ , is produced from a precursor material of  $TiCl_4$ , the  $TiCl_3$  is mixed with aluminium and then heated to a temperature above 300C so that  $AlCl_3$  is formed in the gas phase and the  $AlCl_3$  is condensed away from the reaction zone at a temperature below 200C, leaving in the reaction zone a powder of Ti containing a percentage of aluminium as required for the end product.

In one embodiment the process comprises the steps of heating a precursor material  $TiCl_4$  in a plasma of argon-hydrogen mixtures to produce  $TiCl_3$ , mixing the resulting  $TiCl_3$  powder with aluminium and then heating the mixture to trigger the reaction. The reaction vessel should allow for aluminium chloride to be continuously removed and condensed in a region away from the reaction zone of the titanium chloride and aluminium mixture.  $TiCl_3$ , and aluminium in a powder or a lump form, but preferably in a powder form, are mixed together in a vessel under inert gas or in vacuum. The mixture is then heated to a temperature of several hundred degrees to trigger reaction between the two chemicals, leading to formation of  $AlCl_3(g)$ , and the  $AlCl_3$  is condensed elsewhere in the vessel at a temperature below 200C.

In a further embodiment, the process comprises the steps of heating predetermined amounts of material  $TiCl_4$  and aluminium to form  $TiCl_3$  and  $AlCl_3$ , heating the product mixture to a temperature above 300C and providing for  $AlCl_3$

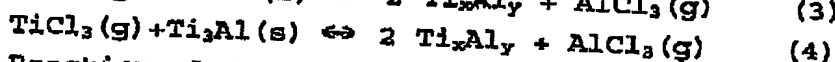
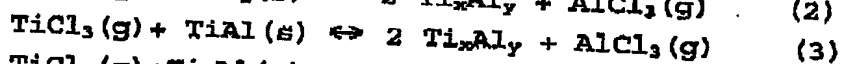
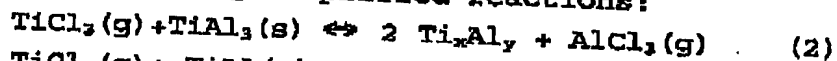
to be evaporated from the reaction zone, driven away from the reaction and condensed away from the reaction zone at a temperature below 200C, adding further aluminium material to the product depending on the required composition, then heating the mixture under the same physical conditions to a temperature above 300C to trigger chemical reactions leading to formation of  $\text{AlCl}_3(\text{g})$  whilst providing for the  $\text{AlCl}_3(\text{g})$  to be condensed elsewhere in the vessel at a temperature below 200C.

Overall reaction between titanium subchlorides  $\text{TiCl}_3$  and Al occur in the following form:



Where Al is in the solid or liquid phase.

The presence of Ti and Al may lead formation of Ti-Al intermetallic compounds such as  $\text{TiAl}_3(\text{s})$ ,  $\text{TiAl}(\text{s})$  and  $\text{Ti}_3\text{Al}(\text{s})$ . Then  $\text{TiCl}_3$  may react with aluminium according to the following simplified reactions:



Reactions 1-4 are driven in the forward direction by continuous removal of  $\text{AlCl}_3$  from the reaction zone. As a result, equilibrium is tilted to the right and the reaction proceeds until completion. We find that the reaction proceeds slowly at temperatures slightly above 200C under an argon atmosphere at 1 atm. The reaction becomes very rapid at temperatures above 500C as the Gibbs free energy of the total reaction becomes negative as seen in Figures 1 and 2. Figure 1 shows the Gibbs energy for  $\text{AlCl}_3$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_3 + \text{Ti-Al}$ . Figure 2 shows the total Gibbs energy for reactions 1-4 leading to formation of solid titanium.

Because of the strong affinity between titanium and aluminium, the presence of Al and Ti may result in formation of titanium-aluminium alloys and/or intermetallic compounds  $\text{Ti}_x\text{Al}_y$ . For these compounds, the Gibbs energy of formation  $\Delta G_f^\circ$  is generally less than

32kJ.mole<sup>-1</sup> for all aluminium concentration up to 80% of the alloys (R.G.Reddy et al. J. Alloys and Compounds, vol 321 (2001) 223).

Figure 2 shows the variation with temperature of the total Gibbs energy for reaction leading to formation of AlCl<sub>3</sub>(g) and Ti(s), starting from TiCl<sub>3</sub> and Al. Also shown in Figure 2, the total Gibbs energy for reaction leading to formation of Ti(s) and AlCl<sub>3</sub>(g), starting from TiCl<sub>3</sub> and Ti-Al compounds. The total Gibbs free energy for Ti-Al is taken to be -32kJ.mole<sup>-1</sup>

It is usually considered that chemical reactions proceed rapidly for negative values of the total Gibbs energy of the reaction. It is seen in Figure 2 that ΔG is negative at temperatures above 800K (525C) for reaction 1. This is in excellent agreement with our observations showing rapid combustion reaction between TiCl<sub>3</sub> and Al at a temperature of 500C, in argon at 1 atm. We find that as the temperature of the mixture TiCl<sub>3</sub>-Al increases above 500C, a cloud of white fume moves from the reaction zone towards the cold region of the vessel where it recondenses forming solid AlCl<sub>3</sub>. For reactions involving Ti-Al compounds, we find that in argon at 1 atm, reactions leading to formation of Ti(s) and Ti<sub>x</sub>Al<sub>y</sub> (reactions 2, 3 and 4) seem to proceed rapidly at temperatures above 850C.

Titanium chlorides may escape from the reaction zone or disproportionate during heating. Gaseous TiCl<sub>3</sub> that may evaporate during the heating process reacts more readily with Al and further enhances formation of Ti compounds. For a mixture of TiCl<sub>3</sub> and Al powder, with [Al]/[TiCl<sub>3</sub>] > 1, we find that only small quantities of less than a few percent of TiCl<sub>3</sub> escapes the reaction zone, and it is recondensed in a region of the vessel at a temperature around 500K and introduced back into the reaction zone, or alternatively collected for reprocessing. TiCl<sub>2</sub> that could be produced due to disproportionation reacts with Al compounds faster than TiCl<sub>3</sub> and enhances reactions leading to formation of Ti compounds. We find no evidence of major

losses due to escape of  $TiCl_4$ , probably because  $TiCl_4$  reacts with Ti leading to formation of  $TiCl_3$ . Our experimental observations suggest that for production of titanium with a high aluminium content, disproportionation reactions are of no significant impact on the efficiency of the process as we are able to account for most of the Ti in the feedstock materials. For production of titanium with a low aluminium content, the initial amount of aluminium used is less than the stoichiometric amount needed to remove all the chlorine from the  $TiCl_3$  materials. The excess titanium chloride remaining after depletion of available aluminium is evaporated from the product and condensed elsewhere for reprocessing.

Production of  $TiCl_3$  can be carried out from  $TiCl_4$  using a hydrogen plasma route or through reduction with aluminium. Production of  $TiCl_3$  in a hydrogen plasma, known as the Huel process has been used in industry for production of catalyst for several decades. Figure 3 shows the composition of  $TiCl_4$ -Hydrogen plasma at temperature between 300K and 5000K. It is seen  $TiCl_4$  can be converted into solid  $TiCl_3$  by reacting it with hydrogen in a plasma. It is also seen that the conversion rate is almost 100%. The energy cost for synthesis of solid  $TiCl_3$  is very low as the overall reaction leading to  $TiCl_3$ :  
 $TiCl_4(g) + (1/2)H_2 \rightleftharpoons Cl_2(s) + HCl$  with  $\Delta H = 50$  KJ/mole.

For reduction of  $TiCl_4$  with Aluminium, the process is usually carried out in closed vessel containing appropriate amounts of  $TiCl_4$  and Al at a temperature above 200C, leading to formation of a mixture of  $TiCl_3$  and  $AlCl_3$ . Pure  $TiCl_3$  is obtained from the mixture by distillation at temperature above 200C and allowing  $AlCl_3$  to condense elsewhere.

For the process disclosed here, production of titanium-aluminium compounds is made by mixing subchlorides, preferably  $TiCl_3$ , with aluminium in a powder form, placing the materials in a vessel under vacuum or

in an inert atmosphere and heating the mixture. For processing under flowing inert gas or under vacuum,  $\text{AlCl}_3$  formed due to reactions described above is driven into a different part of the vessel at a temperature below 200K.

5 The heating continues until the reactions proceed to completion or until complete depletion of available titanium subchlorides and/or aluminium

Figure 4 shows a simple system used to make Ti-Al compounds with different Al contents and compositions.

10 For this configuration, a mixture of  $\text{TiCl}_3$  and Al, 1, is placed into a vessel 2 heated at a temperature higher than 300 C. Reactions between  $\text{TiCl}_3$  and Al in vessel 2 lead to formation of gaseous  $\text{AlCl}_3$ . A stream of argon gas 10 introduced in Vessel 2 carries the gaseous  $\text{AlCl}_3$  together

15 with any titanium chlorides that may escape from the reaction zone and drives them through a second vessel 3 held at a temperature between 300 C and 500 C, so that  $\text{TiCl}_3$  is recondensed while  $\text{AlCl}_3$  remains in the gas phase. Alternatively,  $\text{TiCl}_3$  may be recondensed on the upper walls

20 of vessel 2 if they are held at an appropriate temperature. The remaining  $\text{AlCl}_3$  together with any  $\text{TiCl}_4$  that may have formed in the reaction zone due to disproportionation are driven through vessel 4 at a temperature higher than 136 C and lower than 200 C so that

25  $\text{AlCl}_3$  is recondensed and the remaining  $\text{TiCl}_4$  is driven into vessel 5 held at room temperature. The remaining argon gas is discharged out of the system or recycled.

The  $\text{TiCl}_3$  and an aluminium powder whose relative mass compared to the  $\text{TiCl}_3$  amount depends on the composition of the required product, are introduced into a vessel as

30 described above and then heated until the reaction is complete.

For these processes described above the product is in the form of a fine powder. The powder may be discharged

35 from the vessel at the completion of chemical reactions in the reaction zone for further processing. Alternatively, the powder may be further processed in-situ for production

of other materials. Alternatively the powder may be heated in-situ to make coarse grain powder. In a different embodiment the powder may be compacted and/or heated in-situ and then melted to produce ingot.

5 In one embodiment of the process in accordance with the present invention, a precursor material is mixed with aluminium in a powder or lump form (preferably powder form) and heated to a temperature  $T_1$ , in this embodiment by raising the temperature of the container. The  
10 precursor material, namely  $TiCl_3$ , is in a powder form. The second precursor materials, namely aluminium, may be in the form of a liquid, or a lump solid or a powder (it is preferably in powder form). The materials are placed in a container and heated to trigger reactions between the  
15 Aluminium and the chlorine from the  $TiCl_3$  compounds. In this embodiment the products are in a powder form that may be discharged out of the vessel or may be further reacted with reagents, in a solid, liquid or gas form, in the form of other materials introduced in the reaction zone during  
20 or after processing with aluminium.

A further embodiment of an apparatus which can be used to prepare titanium-aluminium compounds in accordance with the present invention is illustrated in Figure 5. The apparatus in this case is a simple vessel having  
25 relatively long side walls 20. An upper portion 40 of the side walls 20 forms a first condensation zone at temperature  $T_2$ , for condensation of  $AlCl_3$ . A middle portion 50 of the side walls 20 forms a second  
30 condensation zone 50 at temperature  $T_3$  allowing for condensation of  $TiCl_3$ . Titanium aluminium compounds 1 are formed at the bottom of the container.

Parameters influencing reactions in the reaction zone described above include the pressure in the reaction vessel, the temperature of the reaction zone and the grain  
35 size of the Al powder. We find that for operation under low pressure, a lower temperature is required to drive the reaction as  $AlCl_3$  is removed faster from the reaction zone



and  $TiCl_3$  species become more volatile and more active triggering reactions with Aluminium. However, this also results in a lower yield, to escape of volatile titanium chloride, and possibly to production of a two phase product due to disproportionation. Also, we find the reaction between  $TiCl_3$  and Al depends strongly on the size of the Al powder grain. The reaction is much faster for smaller grains and also the yield is higher. Very fine aluminium powder results in formation of a product of Ti-Al compounds with very fine grain having irregular shapes. Also, we have found that with cheaper, less fine powders, the production yield of titanium aluminium compounds is still high and the grain size for the powder is comparable to that for the starting Al powder.

Production of Ti-Al alloys and intermetallic compounds may be carried out using the current process starting from a  $TiCl_4$  feedstock materials as follows.

#### Reduction of $TiCl_4$ using Aluminium:

$TiCl_4$  and aluminium metal in appropriate amounts are introduced into a closed vessel under an argon atmosphere. The vessel is then heated to a temperature above 200C to form a mixture of  $TiCl_3$  and  $AlCl_3$ . The  $TiCl_3$  powder is then extracted from the mixture by distillation as described before. The  $TiCl_3$  powder is then mixed with more aluminium if required and processed utilising an apparatus such as described above in relation to Figure 4.

#### Reduction of $TiCl_4$ using hydrogen and Aluminium:

The precursor materials of  $TiCl_4$  may be fed into a plasma-processing unit operating with argon and hydrogen gas to produce  $TiCl_3$ . Then, products at the exit of the plasma processing system may travel through a filter to separate  $TiCl_3$  from the gas stream and the resulting  $TiCl_3$  powder is then moved into a processing chamber where it is mixed with an appropriate amount of aluminium, depending on the required composition of the end product. The  $TiCl_3$

powder is then mixed with aluminium and processed utilising an apparatus such as described above in relation to Figure 4 or Figure 5. At the completion of the reaction, the materials can be discharged from the reaction vessel for use in manufacturing. Alternatively, the powder can be consolidated in-situ and then melted to produce ingots.

Gases from the plasma system may be re-used after separation and cleaning.

Figure 6 is a schematic diagram of a process for the production of titanium aluminium compound powder from titanium tetrachloride starting materials, in accordance with an embodiment of the present invention. The process discloses how aluminium trichloride can be recycled to produce raw materials.

$\text{TiCl}_4$  is reduced using aluminium or hydrogen as discussed above to  $\text{TiCl}_3$  (step 1). In step 2,  $\text{TiCl}_3$  is reduced by aluminium in accordance with an embodiment of the present invention to produce Ti-Al powders and aluminium tetrachloride.

The aluminium tetrachloride can be electrolysed to produce aluminium and chlorine or used for other purposes (step 3). Advantageously in accordance with the present invention the aluminium chloride can be recycled to produce titanium tetrachloride by reacting  $\text{AlCl}_3$  with the titanium ore (Rutile titanium oxide).  $\text{Al}_2\text{O}_3$  produced by this process can be sold or electrolysed to produce aluminium raw material (step 5).

Figure 7 shows the Gibbs free energy for the half reaction leading to aluminium oxide and titanium tetrachloride. The total Gibbs free energy for reaction leading to the formation of titanium tetrachloride is negative at all temperatures higher than 300K, suggesting the reaction is exothermic.

The method described here may also be used for production of metals and metal alloys by mixing metal halide or a mixture of metal halides (chlorides,

bromides, iodides and fluorides) and carry out the process as described above for the  $TiCl_4$ . For example, zirconium and zirconium alloys may be produced using the same procedures described above for Ti and Ti alloys respectively. For zirconium-based products, the starting material is zirconium chloride. Other examples of metals that can be produced using the present process include vanadium and its alloys and intermetallic compounds. Furthermore, hydrides can also be produced by heating the resulting powder materials in the presence of hydrogen. Also, the process described here can be used for production of nickel aluminides  $Ni_3Al$ ,  $NiAl$  and  $NiAl_3$  and also zirconium aluminides in a powder form.

Titanium metal can be produced by the above process but it may be quite expensive as very fine aluminium powders may be required, resulting in a high production cost.

The present process may be used for production of powders with a controlled particle size of various compositions including compounds of pure metal, oxides, nitrides of elements such as Ti, V and zirconium as described above for titanium. Many other materials may be produced by this chemical process.

Modifications and variations as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for the production of titanium compounds, comprising the steps of mixing a precursor material of titanium trichloride and/or titanium dichloride (titanium subchloride) with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium chlorides and titanium compounds.
2. A method in accordance with claim 1, comprising the step of arranging the conditions to favour a forward reaction to form the aluminium chlorides and titanium compounds, and reduce the reverse reaction.
3. A method in accordance with claim 2, wherein the step of arranging the reaction conditions includes the step of driving aluminium chlorides away from a reaction zone where the aluminium and precursor material are reacting.
4. A method in accordance with claim 3, wherein the step of arranging reaction conditions includes the step of continuous removal of aluminium chloride from the reaction zone.
5. A method in accordance with any one of the preceding claims, comprising the step of preparing the titanium subchloride precursor material from titanium chloride ( $\text{TiCl}_4$ ).
6. A method in accordance in with claim 5, comprising the step of preparing titanium trichloride by reduction of  $\text{TiCl}_4$  using aluminium.
7. A method in accordance with claim 5, wherein the step of preparing titanium trichloride is carried out by heating  $\text{TiCl}_4$  in a plasma or argon-hydrogen mixture.
8. A method in accordance with claim 6 or claim 7, comprising the further step of recycling aluminium chloride produced by the reaction and utilising the aluminium chloride to produce  $\text{TiCl}_4$ .
9. A method in accordance with claim 7, wherein the aluminium chloride is used to reduce titanium oxide to produce  $\text{TiCl}_4$ .

10. A method in accordance with any one of claims 2 to 9, wherein the aluminium chloride is condensed away from the reaction zone at a lower temperature than the temperature of the reactants in the reaction zone.
- 5 11. A method in accordance with any of the preceding claims, wherein any titanium subchloride one escaping the reaction zone is condensed at a temperature different from that in reaction zone.
12. A method in accordance with claim 11, comprising the further step of returning the condensed titanium subchloride to the reaction zone.
- 10 13. A method in accordance with any one of the preceding claims, wherein the precursor material includes vanadium subchlorides, and a product of the reaction is an alloy or intermetallic complex including titanium and vanadium.
- 15 14. A method in accordance with any one of the preceding claims, comprising the further step of adding a reagent to the product of the reaction to produce a further product.
15. A method in accordance with any one of the preceding claims, wherein the precursor material is mixed with a powder of reducing aluminium metal.
- 20 16. A method in accordance with claim 13, wherein the precursor material includes zirconium subchlorides, and a product of the reaction is an alloy or intermetallic complex including zirconium and vanadium.
- 25 17. A method of producing titanium-aluminium compounds, comprising the steps of heating a precursor material of  $TiCl_4$  in a plasma argon-hydrogen mixture to produce  $TiCl_3$ , mixing the resulting  $TiCl_3$  with aluminium and heating the mixture to produce titanium-aluminium compounds and  $AlCl_3$ .
- 30 18. A method of producing titanium-aluminium compounds, comprising the steps of heating  $TiCl_4$  and aluminium to form  $TiCl_3$  and  $AlCl_3$ , heating the mixture to a temperature above 300C and providing for  $AlCl_3$  to be evaporated from the reaction zone, adding further aluminium to the mixture, and heating the mixture to a temperature above 400C to lead to formation of  $AlCl_3$  and titanium-aluminium
- 35

compounds.

19. An apparatus for the production of a metal compound, comprising a reaction vessel including a reaction zone within which a precursor material of metal halide is mixed with aluminium, the mixture being heated to a temperature sufficient such that the precursor material reacts with the aluminium to result in the formation of aluminium halide and a product, and a first condensation zone arranged to be operated to a temperature such that the aluminium halide condenses in the first condensation zone.
20. An apparatus in accordance with claim 18, also providing a second condensation zone arranged to condense metal halide escaping the reaction mixture.
21. An apparatus in accordance with claim 19, the second condensation zone being arranged to return condensed metal halide to the reaction zone.
22. A method for the production of a metal compound, comprising the steps of mixing a precursor material of metal halide with aluminium and heating the mixture to a temperature sufficient such that the precursor material reacts with the aluminium, resulting in the formation of aluminium halide, and arranging the conditions to favour the forward reaction to form the aluminium halide and reduce the reverse reaction.
23. A method in accordance with claim 22, wherein the step of arranging the reaction conditions includes the step of driving aluminium halide away from a reaction zone where the aluminium and precursor material are reacting.
24. A method in accordance with claim 22 or claim 23, wherein the metal halide is titanium tri-chloride, and a product of the reaction includes titanium-aluminium compounds.
25. A method for the production of vanadium and/or vanadium compounds, comprising the steps of mixing a precursor material of vanadium subchloride with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium halides and vanadium and/or

vanadium compounds.

26. A method for the production of zirconium and/or zirconium compounds, comprising the steps of mixing the precursor material of zirconium subhalide with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium halide and zirconium and/or zirconium compounds.

27. A method for the production of titanium and/or titanium compounds, comprising the steps of mixing a precursor material including titanium tri-chloride with a reducing agent and heating the mixture to trigger reactions leading to the formation of chlorides and titanium and/or titanium compounds.

28. A method for producing Ti-Al compounds comprising the steps of heating  $TiCl_4$  and Al powder at temperatures higher than 300 C under flowing conditions, followed by reactions between  $TiCl_3$  and the remaining Al leading to formation of Ti-Al compounds.

29. A method for production of a powder of titanium-aluminium intermetallic compounds  $Ti_3Al$ ,  $TiAl$  and  $TiAl_3$  and alloys based on titanium-aluminium intermetallics according to any one of claims 1 to 18 wherein the starting materials include titanium chloride and aluminium powder.

30. A method for production of a powdered alloys of Ti-Al-X-Y (X,Y = Cr, Nb, Mn, B, Zr, Si, etc), wherein the starting materials include chlorides or powders of X and/or Y.

31. A method for the production of a powder of titanium-aluminium-vanadium alloys, wherein the starting materials include titanium chloride and aluminium powder.

Dated this 21st day of November 2003

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By their Patent Attorneys  
GRIFFITH HACK

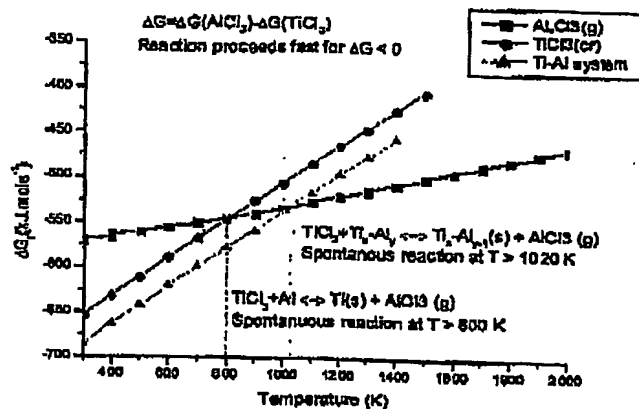
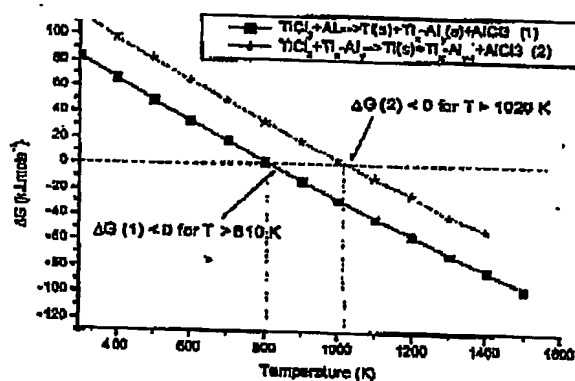


Figure 1: Gibbs energy of formation for  $\text{AlCl}_3(\text{g})$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_3\text{-Ti-Al}$ .



Total Gibbs free energy for reactions leading to formation of  $\text{Ti}(\text{s})$

FIGURE 2.



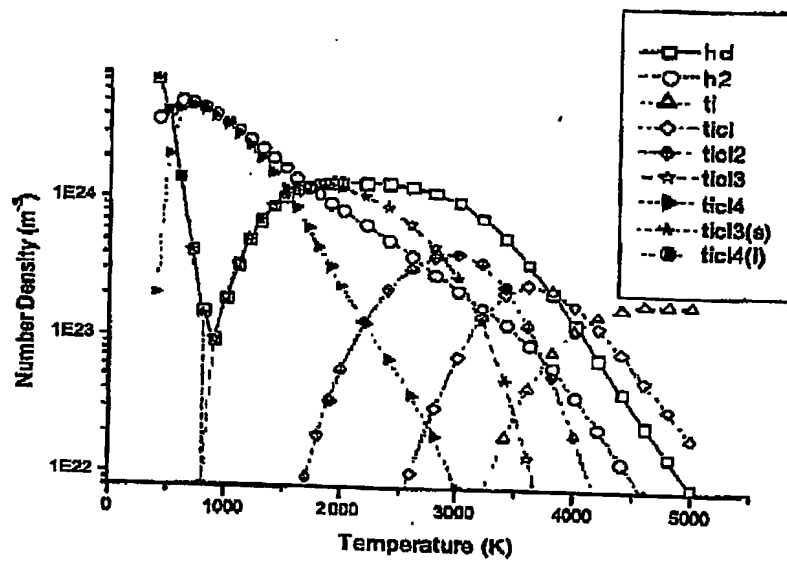


Figure 3: Equilibrium composition of Hydrogen-TiCl<sub>4</sub> plasma at 1 atm. 1 mole of TiCl<sub>4</sub> and 1 mole of H<sub>2</sub>.

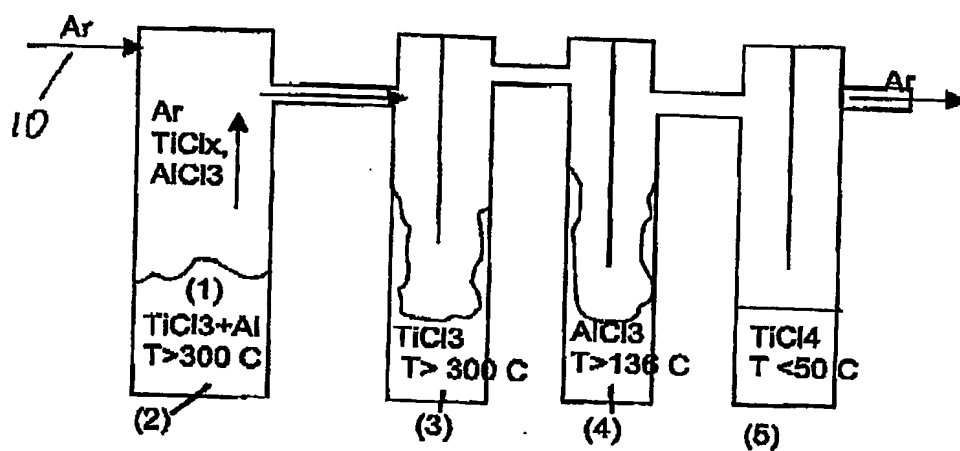


Figure 4: A Schematic diagram of an apparatus for carrying out the process.

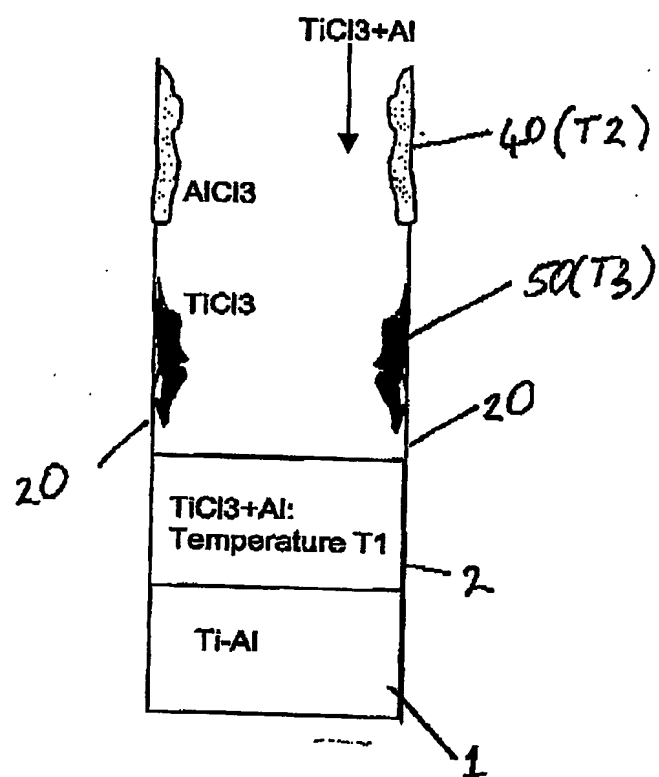
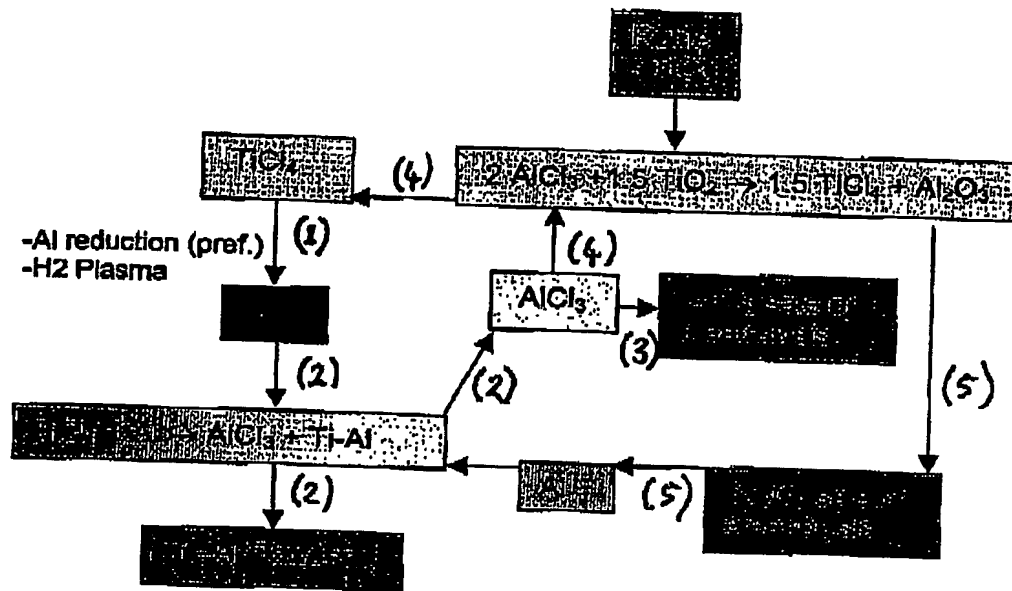
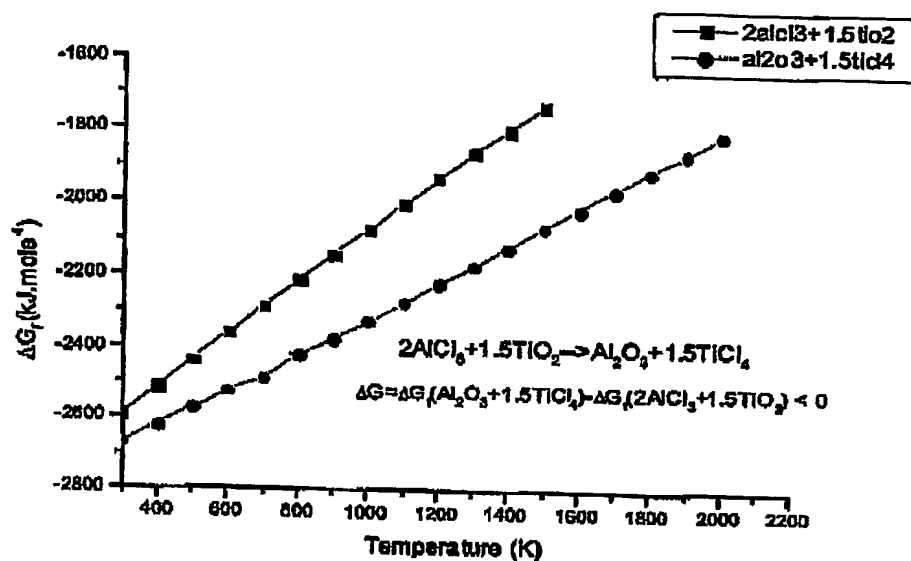


FIGURE 5



A schematic diagram illustrating production of Ti-Al powder from TiCl<sub>4</sub> starting materials.

FIGURE 6



Gibbs free energy for half reactions (2 AlCl<sub>3</sub> + 1.5 TiO<sub>2</sub>) and (Al<sub>2</sub>O<sub>3</sub> + 1.5 TiCl<sub>4</sub>). Total Gibbs free energy for reaction leading to formation of TiCl<sub>4</sub> is negative at all temperatures higher than 300 K, suggesting the reaction is exothermic.

Figure 7